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(54) Title: HOLLOW BEADS OF POLYETHYLENE

(57) Abstract: The present invention discloses a method for preparing hollow beads of polyethylene of controlled morphology and size.

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HOLLOW BEADS OF POLYETHYLENE.

5

This invention is related to the field of hollow beads of polyethylene and their method of preparation. It also relates to the catalyst components used in their preparation.

10

Iron-based catalyst systems have been described in literature for the polymerization or oligomerisation of olefins.

For example by Britovsek et al. (G.J.P. Britovsek, V.C. Gibson, B.S. Kimberlay, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White and D.J. Williams, in Chem. Comm. , 1998, 849.) describe novel olefin polymerization catalysts based on iron and cobalt that are active for the polymerization of olefins, particularly ethylene.

Small, Brookhart and Bennett (B.L. Small, M. Brookhart and A.M.A. Bennett, in J. Am. Chem. Soc., 1998, 4049.) describe an iron and cobalt catalysts that are very active for the polymerisation of ethylene.

Small and Brookhart (B.L. Small and M. Brookhart, in Macromolecules, 1999, 2120.) disclose a new generation of Iron catalysts for the polymerization of propylene.

Some other research groups such as for example Roscoe et al. (S.B. Roscoe, J.M. Fréchet, J.F. Walzer and A.J. Dias, in Science, 1998, vol. 280, 270.) have been able to produce polyolefin spheres from metallocenes supported on non-interacting polystyrene support.

Liu and Jin (C. Liu and G. Jin, in New J. Chem. 2002, 1485.) disclose a method for immobilizing an iron-based catalyst on polystyrene chains.

None of these prior art documents have addressed the problem of preparing hollow beads of polyethylene of controlled morphology and size.

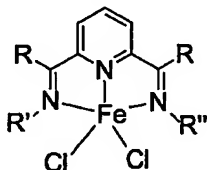
The present invention discloses a method for preparing hollow beads of polyethylene of controlled morphology and size.

The present invention also discloses a supported iron-based catalyst component very active in the preparation hollow beads of polyethylene.

10 The present invention further discloses a method for preparing the supported iron-based catalyst component.

Accordingly, the present invention discloses a method for preparing hollow beads of polyethylene of controlled morphology and size that comprises the steps of:

15 a) providing a supported catalyst component wherein the support is a porous functionalised bead of polystyrene and wherein the catalyst component is covalently bound to the support and is an iron based complex of general formula I



20

(I)

wherein R is the same and is an alkyl having from 1 to 20 carbon atoms and wherein R' and R'' are the same or different and are a substituted or unsubstituted alkyl having from 1 to 20 carbon atoms, or a substituted or

25

substituted aryl having substituents from 1 to 20 carbon atoms;
b) activating the supported catalyst with a suitable activating agent;
c) feeding the ethylene monomer;

- d) maintaining under polymerization conditions;
- e) retrieving hollow beads of polyethylene of controlled morphology and size.

5 R are the same and are preferably an alkyl having from 1 to 4 carbon atoms, more preferably, it is methyl.

R' and R'' are the same or different and are selected from a substituted or unsubstituted alkyl having from 1 to 6 carbon atoms or are a unsubstituted or substituted aryl having substituents from 1 to 6 carbon atoms. Preferably, R' and R''
10 are the same and are phenyls. The substituents on the phenyls, if present, can have either an inductive attracting, donating effect or a steric effect.

The substituents that have an inductive attracting or donating effect can be selected from hydrogen or an alkoxy, or NO₂, or CN, or CO₂R or an alkyl having
15 from 1 to 20 carbon atoms, or a halogen or CX₃ wherein X is a halogen, preferably fluor, or a fused ring between positions 3 and 4, or between positions 4 and 5 or between positions 5 and 6.

The steric environment of the iron-based complex is determined by the substituents
20 at positions 2 and 6 and optionally at positions 3, 4 and 5 on the phenyls.

For the steric effect, the preferred substituents on the phenyls, if present, can be selected from tert-butyl, isopropyl or methyl. The most preferred substituents are isopropyl in positions 2 and 6 or methyl in positions 2, 4 and 6.

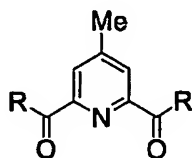
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The present invention discloses a supported catalyst component, very active in the preparation of hollow beads of polyethylene of controlled morphology and size, that comprises a support prepared from a porous bead of functionalised polystyrene and an iron-based complex covalently bound to the support by a flexible arm, said
30 flexible arm being a substituted or unsubstituted alkyl having a length of from 2 to 18 carbon atoms.

Preferably the flexible arm is an unsubstituted alkyl having from 3 to 6 carbon atoms.

The present invention also discloses a method for preparing the supported catalyst
5 component that comprises the steps of:

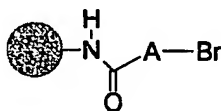
a) providing a first component of general formula II



(II)

10 wherein R is the same and is an alkyl having from 1 to 20 carbon atoms;

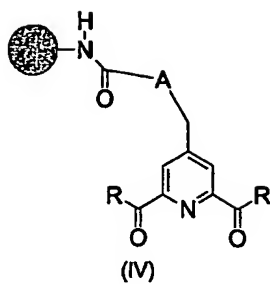
b) providing a porous functionalised bead of polystyrene of the general formula
III



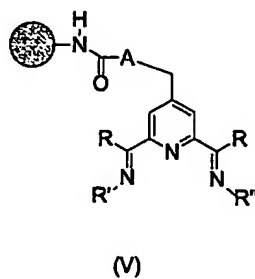
(III)

15 wherein the flexible arm A is a substituted or unsubstituted alkyl having from 2 to 18 carbon atoms;

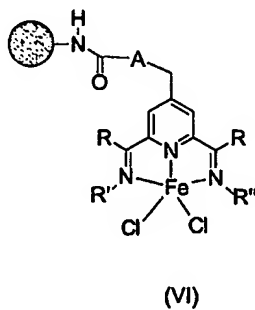
c) creating a covalent bond between the component of step a) and the porous functionalised bead of step b) to produce a complex of formula IV



- d) reacting the supported component of step c) with a first alkyl- or aryl-amine $R'-NH_2$ and with a second alkyl- or aryl-amine $R''-NH_2$, wherein R' and R'' are the same or different, to prepare a bis-imine complex of formula V;



- e) reacting the bis-imine complex of step d) with ferric chloride ($FeCl_3$) in a THF to coordinate the ferric centre and obtain a catalyst component of the general formula VI



All reactions of step e) are carried out under inert atmosphere at room temperature of about 20 °C and under atmospheric pressure. The solvent is then evaporated and dry beads of the supported catalyst component are retrieved.

5

The starting porous functionalised beads of polystyrene have a size of from 250 to 500 microns and they are prepared from cross linked polystyrene wherein the degree of cross linking is ranging from 0.5 to 5 %. A proper level of cross linking must be selected: it must be sufficiently high to insure shape constraint but
10 sufficiently low to allow absorption of the active ingredients. A degree of cross linking of from 1 to 2 % is preferred.

A study of the finished supported iron-based catalyst component reveals that the distribution of iron within the compound is not homogeneous: there is a decreasing
15 concentration when going from the surface to the center of the bead as seen in Figure 1 representing a cross section of a bead of catalyst component.

A catalyst system is then prepared by activating the supported catalyst component with a suitable activating agent.

20

The activating agent can be selected from aluminoxanes or aluminium.

The aluminium alkyls are of the formula AlR_x and can be used wherein each R is the same or different and is selected from halides or from alkoxy or alkyl groups
25 having from 1 to 12 carbon atoms and x is from 1 to 3. Especially suitable aluminiumalkyl are dialkylaluminum chloride, the most preferred being diethylaluminum chloride (Et_2AlCl).

Aluminoxane is used to activate the catalyst component during the polymerisation
30 procedure, and any aluminoxane known in the art is suitable.

The preferred aluminoxanes comprise oligomeric linear and/or cyclic alkyl aluminoxanes represented by the formula :

$R-(Al-O)_n-AlR_2$ for oligomeric, linear aluminoxanes



and

5

$(-Al-O)_m$ for oligomeric, cyclic aluminoxanes,



- 10 wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C₁-C₈ alkyl group and preferably methyl.
Methylaluminoxane (MAO) is preferably used.

- 15 Preferably the activating agent is added in excess to the dry beads of supported catalyst component. The molar ratio [Al] : [Fe] is at least 2000, preferably, at least 2500.

- 20 The hollow beads of polyethylene have a diameter of from 0.5 to 5 mm as can be seen on Figure 2 representing the starting beads of polystyrene and the final beads of polyethylene. The diameter of the hollow beads of polyethylene depends upon the nature of the substituents attached to the phenyl groups R' and R'' of the iron-base catalyst component as can be seen on Figure 3 representing the final beads of polyethylene obtained with various substituents on the phenyl groups. In addition, the beads have a very narrow size distribution.

25

The catalytic activity is also governed by the nature of the substituents R' and R'' on the phenyl groups.

List of Figures.

30

Figure 1 represents respectively the percentages of iron and of chlorine as a function of distance from the surface along a diameter of a bead of catalyst

component measured by a scanning electron microscope (SEM) equipped with a energy dispersive X-ray spectrometer (EDS).

Figure 2 represents the starting polystyrene beads and the final polyethylene
5 hollow beads.

Figure 3 represents the final polyethylene beads obtained with various substituents on the phenyl groups. The substituents are respectively: isopropyl, diisopropyl, tert-butyl, trimethyl, diethyl and dimethyl.

10

Figure 4 represents a hollow bead of polyethylene. Figure 4a is an external view and Figure 4b is an internal view of the bead.

Figure 5 represents the reflectance spectrum of catalyst VI expressed in % as a
15 function of wave number expressed in cm^{-1} .

Examples.

The starting materials and reagents, purchased from commercial suppliers, were
20 used after standard purifications. The solvents were dried and distilled before use as follows:

- over sodium and benzophenone for toluene and tetrahydrofuran (THF),
- over sodium for methanol and
- over phosphorus pentoxide for dichloromethane (DCM)).

25 Manipulations were all performed on a vacuum line under argon, using standard Schlenk techniques and glove box techniques.

The rotating shaker is a Labquake shaker.

NMR spectra were recorded on a Bruker DPX 200 at 200 MHz (for ^1H) and 50MHz (for ^{13}C).

30 Infrared ATR (silicium) spectra were recorded in the range $4000\text{--}400\text{ cm}^{-1}$ on a IR Centaurus microscope.

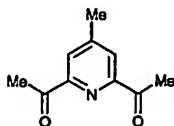
High resolution mass spectra were obtained on a Varian MAT 311 (electronic ionisation mode) at CRMPO, University of Rennes.

Elemental analysis were performed by the CNRS laboratory, Vernaison (France).

Synthesis of the catalyst.

5

The starting compound 2,6-diacetyl-4-methylpyridine (1) was synthesized according to known methods (see for example T.L. Gilchrist and T.G. Roberts, in J. Chem. Soc., Perkins Trans., 1983, 1283, or T.L. Gilchrist, D. Hughes, W. Stretch and W.J.T. Crystal, in J. Chem. Soc., Perkins Trans., 1987, 2505.)

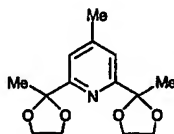


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(1)

1.22 g (6.89 mmol) of 2,6-diacetyl-4-methylpyridine (1) were dissolved in 120 ml of dichloromethane (DCM). 2.10 g (11.03 mmol) of para-toluene sulfonic acid were then added followed by 5.2 ml (93.74 mmol) of ethylene glycol. The reaction mixture was stirred at reflux for 3 days at 50 °C. It was then cooled to room temperature, dissolved in 50 ml of DCM, washed twice with 200 ml of saturated NaHCO₃ and three times with 200 ml of water. The organic phase was dried over magnesium sulfate, filtered and dried under reduced pressure. A column chromatography (silica, DCM as eluent) afforded 1.244 g (4.7 mmol) of compound (2) in 68% yield, as a yellow oil.

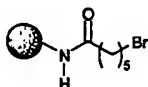
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(2)

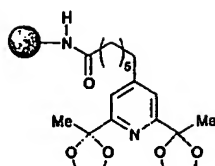
Under argon, to 200 mg (0.2 mmol) of polystyrene AM-NH₂ beads purchased from Rapp Polymere (1mmole/g, size from 250 to 315 microns) in 3.6 mL of dichloromethane (DCM), 0.44 mL (3.0 mmol) of triethylamine were slowly added, followed by the careful addition of 0.36 mL (2.4 mmol) of 6-bromohexanoyl chloride. The reaction mixture was stirred for 2 h at room temperature on a rotating shaker before being drained. The beads were then washed twice for 30 minutes with dimethylformamide, twice for 10 minutes with DCM, twice for 10 minutes with methanol, twice for 30 minutes with dimethylformamide, twice for 10 minutes with DCM, twice for 30 minutes with methanol and dried under reduced pressure to give 0.2 mmol of the white beads (3). A Kaiser test was performed to verify that the reaction was complete.



15

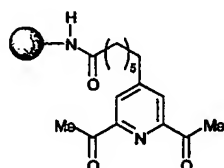
(3)

A solution of lithium diisopropylamine (LDA) was prepared by adding dropwise 0.5 mL (0.66 mmol) of n-butyllithium to a solution, at -20°C, of 0.1 mL (0.72 mmol) of diisopropylamine in 2.2 mL of THF. The dark red solution was stirred at -20°C for 15 min before being added dropwise to a solution also at -20°C, of 160 mg (0.60 mmol) of complex (2) in 2.2 mL of THF. The orange solution was stirred at -20°C for 30 min before being added to 0.2 mmol of the beads (3), under argon. The beads were stirred at room temperature on a rotating shaker overnight. The beads were then washed with twice for 10 minutes and once for 30 minutes in THF, twice for 10 minutes in dimethylformamide, twice for 5 minutes in DCM, once for 90 minutes in methanol, once for 15 minutes in THF, once for 15 minutes in methanol, once for 15 minutes in THF and then dried under reduced pressure. The procedure was repeated a second time to give 0.2 mmol of the dark yellow beads (4).



(4)

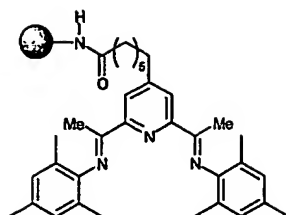
The deprotection of the beads (4) was performed by dissolving 0.2 mmol of
5 beads (4) in 4 mL of THF in which 2 mL of 10% aqueous HCl were added. The
beads became orange. They were stirred at room temperature overnight on a
rotating shaker. They were then drained, washed twice for 30 minutes with a 1/1
mixture of THF/water, twice for 15 minutes with methanol, twice for 30 minutes with
the 1/1 mixture of THF/water, twice for 15 minutes with methanol and then dried
10 under reduced pressure. The procedure was repeated a second time to give the
pale yellow beads (5).



(5)

15

To a mixture of 0.033 mmol of beads (5) in 0.9 mL of DCM were added 0.028
mL (0.198 mmol) of 2,4,6-trimethylaniline and 1 drop of glacial acetic acid. The
beads were stirred at room temperature for 40 h on a rotating shaker. They were
then drained, washed twice for 30 minutes with DCM, twice for 30 minutes with
20 methanol and again with DCM respectively for 30 minutes and 2 hours, twice for 30
minutes with methanol and then dried under reduced pressure. The procedure was
repeated a second time to give the pale yellow beads (6).



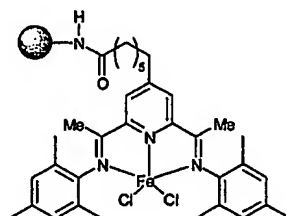
(6)

5 The following reaction was entirely performed in a glove box. A 4.9×10^{-2} M solution of iron(II) dichloride tetrahydrated in DCM and THF was prepared by dissolving 39 mg (0.196 mmol) of iron(II) dichloride tetrahydrated in 1 mL of DCM followed by the addition of 3 mL of THF. To a mixture of 0.01 mmol of beads (6) in 0.3 mL of THF were then added 0.2 mL (0.0098 mmol) of the solution of iron(II)

10 dichloride tetrahydrated. The dark blue beads were stirred at room temperature for 20 h on a rotating shaker. They were then drained, washed once for one hour and twice for 30 minutes with THF, once for 30 minutes and once for one hour with toluene and then dried under reduced pressure to afford the dark blue beads (7), which were stored in a glove box. The amount of iron was measured as :

15 Fe (ICP AES) : 2.61 %

Total loading of beads (7) : 0.467 mmol Fe/ g of beads



(7)

The reflectance spectrum of complex (7) is displayed in Figure 5 representing the reflectance as a function of wave number.

5

Polymerisation of ethylene.

Example 1.

- 10 12.91 mg (6.03 μ mol) of beads (7) in 2 mL of toluene were placed in a 200 mL reactor, which was then flushed with argon for 5 min. Under argon, 5 mL of methylaluminoxane (MAO) (30 % in toluene, 3500 eq.) were added, followed by 85 mL of toluene and the reactor was flushed with argon for 5 min. The temperature was raised to 50°C, the reactor was put under 20 bar of ethylene and the reaction
- 15 mixture was stirred for 17 h. When the reaction mixture was back to room temperature and under argon, the solution was taken off, the beads were washed with ethanol and dried under reduced pressure to give 4.571 g of balls of polyethylene. The activity of beads (7) was measured in grams of polyethylene per mmole of Fe. These methods gave respectively:
- 20 Activity (g polymer/ mmole Fe) = 758
Residual Iron by ICP AES on polyethylene beads: 0.019 %

Example 2.

25

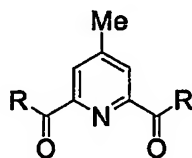
- 2.9 mg (1.35 μ mol) of beads (7) in 2 mL of toluene were placed in a 200 mL reactor, which was then flushed with argon for 5 min. Under argon, 5 mL of MAO (30 % in toluene, 16500 eq.) were added, followed by 85 mL of toluene and the reactor was flushed with argon for 5 min. The temperature was raised to 50°C, the
- 30 reactor was put under 20 bar of ethylene and the reaction mixture was stirred for 3 h. When the reaction mixture was back to room temperature and under argon the solution was taken off, the beads were washed with ethanol and dried under reduced pressure to give 1.874 g of balls of polyethylene. The activity was:

Activity (g polymer/ mmole Fe) = 1388

CLAIMS.

- 5 1. A method for preparing a supported catalyst component for the production of hollow beads of polyethylene of controlled size and morphology that comprises the step of:

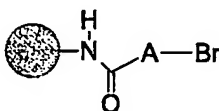
a) providing a first component of general formula II



(II)

wherein R is the same and is an alkyl having from 1 to 20 carbon atoms;

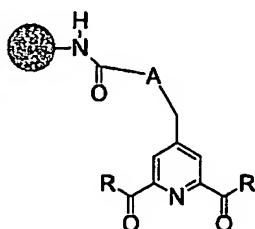
b) providing a porous functionalised bead of polystyrene of the general formula III



(III)

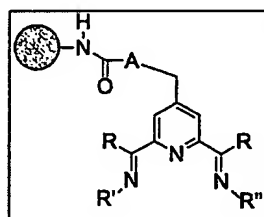
wherein the flexible arm A is a substituted or unsubstituted alkyl having from 2 to 18 carbon atoms;

- c) creating a covalent bond between the component of step a) and the porous functionalised bead of step b) to produce a complex of formula IV



5

- d) reacting the supported component of step c) with a first alkyl- or aryl-amine $R'-NH_2$ and with a second alkyl- or aryl-amine $R''-NH_2$ wherein R' and R'' are the same or different, to prepare a bis-imine complex of general formula V

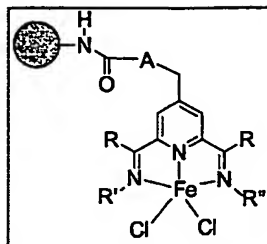


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(V)

- e) reacting the bis-imine of step d) with ferric chloride $FeCl_3$ in a solvent to obtain the final catalyst component of general formula VI

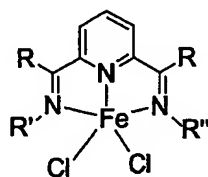
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(VI)

2. The method of claim 1 wherein flexible arm A contains from 3 to 6 carbon atoms.
3. The method of claim 1 wherein the R are the same and are alkyl groups having from 1 to 4 carbon atoms.
4. The method according to any one of claims 1 to 3 wherein R' and R'' in the alkyl- or aryl-amines are the same and are substituted or unsubstituted phenyls.
5. The method of claim 4 wherein the phenyls are substituted with isopropyl groups at positions 2 and 6.
6. The method of claim 4 wherein the phenyls are substituted with methyl groups at positions 2, 4 and 6.
7. A supported catalytic component obtainable by the method according to any one of claims 1 to 6.
8. A method for preparing hollow beads of polyethylene of controlled size and morphology that comprises the steps of:

- a) providing a supported catalyst component as prepared in any one of claims 1 to 6, wherein the support is a porous functionalised bead of polystyrene and wherein the catalyst component is covalently bound to the support and is an Iron-based complex of the general formula I



5

(I)

wherein R, R' and R'' are as defined in any one of claims 1 to 6;

- b) activating the supported catalyst component with a suitable activating agent;
- c) feeding the ethylene monomer;
- d) maintaining under polymerisation conditions;
- e) retrieving hollow beads of polyethylene of controlled shape and size.

10

9. The method of claim 8 wherein the activating agent is methylaluminoxane.

15

10. Hollow beads of polyethylene of controlled morphology and size obtainable by the method of claim 8 or claim 9.

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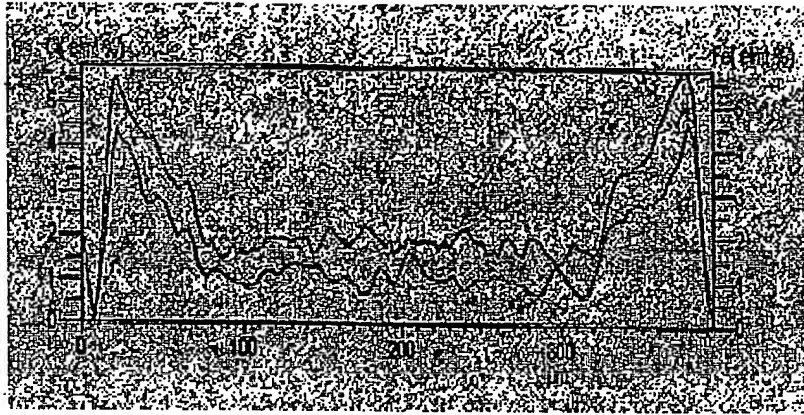


FIGURE 1



FIGURE 2

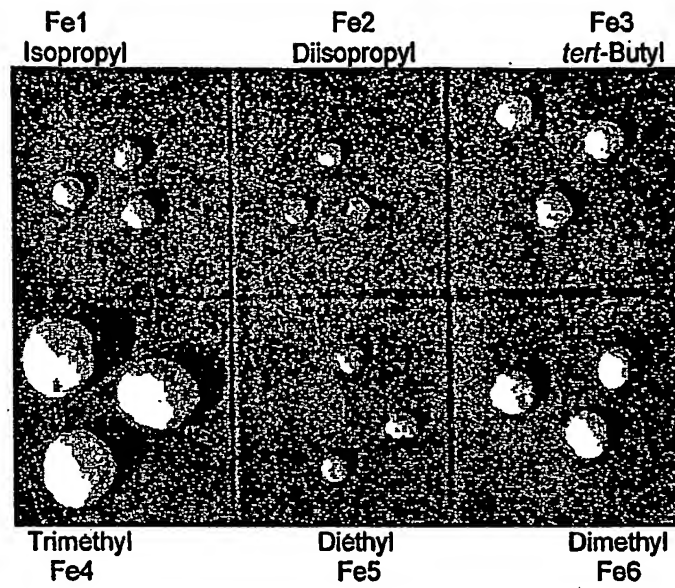


FIGURE 3

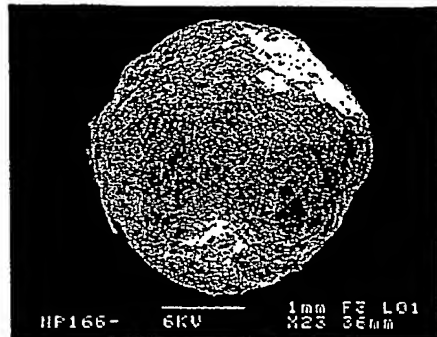


FIGURE 4a

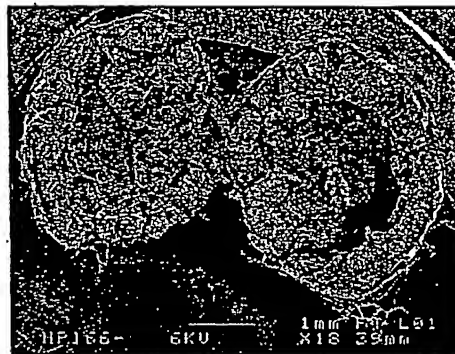


FIGURE 4b

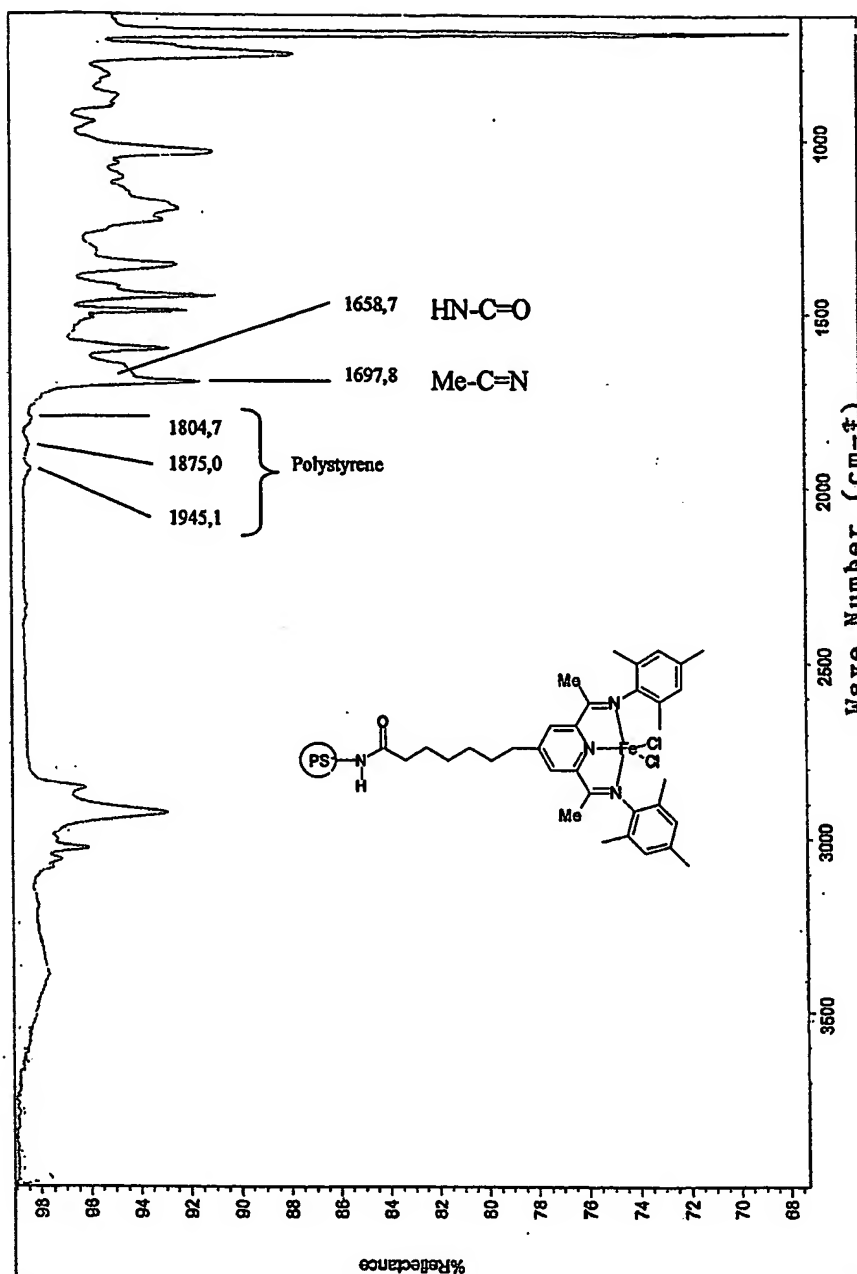


FIGURE 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/050481

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F110/02 C08F4/70 C07F15/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CAPLUS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; LIU, CHANGKUN ET AL: "Preparation of post-metallocene macromolecular catalyst for olefin polymerization" XP002295458 retrieved from STN Database accession no. 2002:499550 abstract & CN 1 306 012 CN (CHANGCHUN INST. OF APPLIED CHEMISTRY, CHINESE ACADEMY OF SCIENCES, PEO) 13 July 2004 (2004-07-13)</p> <p style="text-align: center;">-/-</p>	1-10

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

8 September 2004

Date of mailing of the international search report

20/09/2004

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Parry, J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/050481

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CAPLUS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; JIN, GUOXIN ET AL: "Preparation of unsymmetric post-metallocene macromolecular catalysts for olefin polymerization" XP002295459 retrieved from STN Database accession no. 2002:499551 abstract & CN 1 306 013 CN (CHANGCHUN INST.. OF APPLIED CHEMISTRY, CHINESE ACADEMY OF SCIENCES, PEO) 27 December 2004 (2004-12-27)	1-10
X	LIU C ET AL: "POLYMER-INCORPORATED IRON CATALYSTS FOR ETHYLENE POLYMERIZATION-A NEW APPROACH TO IMMOBILIZE IRON OLEFIN CATALYSTS ON POLYSTYRENE CHAINS" NEW JOURNAL OF CHEMISTRY, CNRS-GAUTHIER-VILLARS, MONTROUGE, FR, vol. 26, no. 10, 2002, pages 1485-1489, XP008017403 ISSN: 1144-0546 cited in the application table 1	10
A	BENVENUTI F ET AL: "NOVEL POLYMER-SUPPORTED BETA-DIKETONATE NICKEL CATALYSTS FOR ALPHA-OLEFIN ACTIVATION" POLYMERS FOR ADVANCED TECHNOLOGIES, JOHN WILEY AND SONS, CHICHESTER, GB, vol. 9, no. 2, 1 February 1998 (1998-02-01), pages 113-120, XP000733424 ISSN: 1042-7147 page 115	1-10
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INTERNATIONAL SEARCH REPORT

International Application No
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